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CHROMOPHORES WITH AUXOCHROME-LIKE FUNCTION

H. Kauffmann

Translation of "Chromophore mit auxochromähnlicher Funktion," Berichte der Deutschen Chemischen Gesellschaft, (German Chemistry Society, Reports), No. 50, 1917, pp. 515-529

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16. Abstract

Chromophores exist which can exert an auxochromic effect in addition to their chromophoric one. Styryl and cyan radicals are given particular attention. Two rules are developed. Numerous chromophores were checked and those with auxochromic functions are described and tabulated.

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CHROMOPHORES WITH AUXOCHROME-LIKE FUNCTION

H. Kauffmann

1. From the fact that on the one hand nitro- /515* derivatives of stilbene are colored, and on the other hand stilbene itself has a violet luminescence capacity, a good while ago[1] I already concluded that the monovalent radical styryl, .CH:CH.C_6H_5, was equipped with auxochrome-like properties. As with the inclusion of true auxochromes in nitro- and dinitrobenzene, inclusion of styryl also yields yellow substances. To clarify and verify this interpretation, with various collaborators I conducted investigations which gradually led us more and more to include other atom groups as well in our considerations. The interpretation proved entirely justified, and led to a finding that chromophores exist which can exert an auxochromic effect in addition to their chromophoric one. /516

2. The task was approached by first studying the influence of styryl on fluorescence. This influence is clearly apparent with even the simplest of the studied substances, stilbene itself, which can of course be considered a styryl-substituted benzene. Like that of a true typical auxochrome, it consists in a shift of the ultraviolet fluorescence of the benzene nucleus towards the limits of the visible range of the spectrum. The eye can recognize a weak violet fluorescence in an alcoholic stilbene solution; as photographs show, this extends as a narrow band into the adjacent ultraviolet. The violet fluorescence is strongly apparent with solid stilbene.

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[1] Die Valenzlehre [Valency Theory], p. 496 (Stuttgart, Verlag von F. Enke, 1911).

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*Numbers in the margin indicate pagination in the foreign text.

This proof is not sufficient. The fluorescence of the stilbene solution is not strong in the ultraviolet, either, and suggests the objection that perhaps styryl functions only as a chromophore, e.g. like cyan. As Ley and von Engelhardt observed,[2] benzonitrile still fully shows the ultraviolet fluorescence of the benzene nucleus, which as with stilbene is shifted towards longer wavelengths than for benzene. Thus cyan apparently by no means joins the great majority of chromophores whose inclusion in benzene completely or almost completely extinguishes the fluorescence of the nucleus. Nevertheless, it is an indubitable chromophore and at best only a very weak auxochrome, for otherwise the nitro-benzonitriles would have to be colored substances.

3. More detailed proof is based on the law of distribution of auxochromes[3] and clearly manifests the difference between styryl and cyan. We do not need the entire law of distribution, but only the portion referring to chromophore-free benzene derivatives, which reads as follows: "If one introduces a second typical auxochrome in benzene in the para position to one already present, fluorescence will also occur in this di-derivative; it is shifted still further towards longer wavelengths and is very intense."

If a second cyan group in para position is introduced into benzonitrile, one gets a substance that presents no fluorescence when studied under the same conditions. With Herr Weischedel I tested this nitrile of terephthalic acid, but with a 15-minute minute exposure of an n/1000 alcoholic solution under /517

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[2]Ph. Ch. 74, 39 (1910).

[3]Z. El. Ch. 18, 481 (1912). -- Die Valenzlehre, p. 504. -- See also: B. 39, 2722 (1906); 44, 2386 (1911). -- More recent works on the law of distribution of auxochromes have unfortunately not been published yet because of the war.

mercury light I could perceive no effect on the photographic plate. Accordingly cyan does after all belong to the chromophores which extinguish the fluorescence of the nucleus; but the extinguishing influence is not as highly developed, and thus the group must be introduced twice.

Styryl is very different. With A. Jeutter I produced p-distyrylbenzene:

$$p\text{-}C_6H_5.CH{:}CH.C_6H_4.CH{:}CH.C_6H_5\text{-}p$$

thus obtaining a new colored hydrocarbon with superb fluorescence capacity. The substance is easily produced from terephthalaldehyde with magnesium benzyl chloride. It forms pale yellow crystals with a yellow-green fluorescence[4] and lends the solvents a brilliant blue-violet fluorescence which is extremely intense even at higher temperatures. This splendid fluorescence, extending far into the visible range, is direct and handsome proof that styryl must be categorized among the auxochromes.

4. The luminophore -- i.e. the seat of emission capacity -- must be considered the middle ring of the compound. This opinion is based on the persistence of fluorescence during stepwise replacement of both styryls with true auxochromes. If both styryls are replaced, one gets compounds with two auxochromes in para position to one another, i.e. substances whose fluorescent capacity has long been known. Thus we only had to study the case of replacing a single styryl. I chose the group $N(CH_3)_2$ as the substituting auxochrome, and thus subjected p-diethylamino stilbene to more extensive testing. This substance was already produced 12 years ago by Franz Sachs and Ludwig Sachs,[5] but they gave no data about its fluorescence. In fact it is characterized by a very high fluorescence capacity; it fluoresces rather strongly greenish-blue[4] in the solid state, and blue to violet in

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[4]Observed behind the blue pane.

[5]B. 38, 515 (1905).

solutions. It has a marked change of fluorescence due to its amino group; in alcohols it fluoresces an intense blue and more violet in indifferent solvents.

5. Despite its auxochrome-like character, however, styryl also belongs to the chromophores. This results first from the well-known fact that inclusion of true auxochromes in stilbene can produce color -- 2,4-diaminostilbene is bright yellow[6] /518 -- but now also from the finding that p-distyrylbenzene is not white but clearly yellow. Thus styryl is an atom group in which auxochromic and chromophoric functions are combined.

The chromophoric properties of styryl are as weak as its auxochromic properties are strong. Thus p-dimethylamino stilbene is still white, and 1,3-distyryl-2,4-diamino benzene[7] is only light yellow, although it even has two styryl chromophores. This situation raises the question whether performing one function inhibits the other. To answer this question (presumably in the negative) particularly requires a search for further such chromophores and particularly a derivation of general rules to promote establishment of quantitative relationships.

6. Considering that cyan has only a slight fluorescence-triggering effect, I hoped by introducing cyan into styryl to obtain a new chromophore whose auxochromic character could be clarified by fluorescence studies. I was not disappointed. This new chromophore, produced by combination, is the residue $.CH:C(CN).C_6H_5$ of α-phenyl-acrylic acid nitrile, here called simply cyan-styryl for short. The compound of main interest here, which has it twice in para position to itself -- namely dicyan-distyrylbenzene:

$$p\text{-}C_6H_5(CN).C:CH.C_6H_4.CH:C(CN).C_6H_5\text{-}p$$

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[6]J. Thiele and R. Escales, B. 34, 2844 (1901).

[7]W. Borosche, A. 386, 351 (1912).

forms easily when terephthalaldehyde is condensed with benzyl cyanide. The product is lemon yellow and in the solid state presents a brilliant yellow fluorescence.[8]

α-Phenyl-cinnamic acid nitrile, $C_6H_5.CH:C(CN).C_6H_5$, which contains only one cyan-styryl, does not fluoresce.[9] The fluorescence of the benzene nucleus is thus suppressed to indetectability by a single inclusion of this chromophoric atom group; but since it resurges with new strength with a further inclusion, cyan-styryl must be considered an auxochrome. In the dissolved state as well, dicyan-distyrylbenzene shows fluorescence, e.g. blue in benzene and chloroform. /519

In other compounds as well, cyan-styryl reveals its auxochromic functions. Included in nitrobenzene, it generates a strongly colored substance, orange-colored p-nitro-α-phenyl-cinnamic acid nitrile, $NO_2.C_6H_4.CH:C(CN).C_6H_5$, and considering that p-nitro-dimethylaniline is only yellow, has a still stronger auxochromic effect than does the $N(CH_3)_2$ group. To make sure that the coloring of this compound, already described by H.V. Frost,[10] is not produced by impurities, I recrystallized it repeatedly from various solvents with and without addition of coal tar, but noted no brightening.

7. To learn the chromophoric properties of cyan-styryl, I asked E. Meyer to produce p-dimethylamino-α-phenyl cinnamic acid nitrile:

$$(CH_3)_2N.C_6H_4.CH:C(CN).C_6H_5.$$

The substance, which we easily obtained from dimethylamino

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[8]Observed behind the blue pane.

[9]As comparison with stilbene indicates, the fluorescence of this substance should roughly be in the blue.

[10]A. 250, 161 (1889). I found the melting point somewhat higher, i.e. 119°[C].

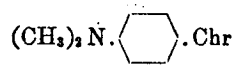
benzaldehyde and benzyl cyanide, is already characterized by an intense, lemon yellow color -- in contrast to the still white, cyan-free, analogous stilbene derivative. The alcohol solution is likewise yellow and in spectrographic examination presents an absorption band starting in the blue, with a maximum around 385 μμ. The inclusion of cyan thus sharply increased the chromophoric functions of the styryl skeleton.

In its solid state, p-dimethylamino-α-phenyl cinnamic acid nitrile has an extraordinary fluorescent capacity. The crystal flakes fluoresce a brilliant yellow-green even in diffuse daylight, with a brightness comparable to that of barium platinum cyanide. Fluorescent screens produced with the substance are well suited for handsome luminescence experiments and even at a distance of 12 cm from 5 g radium bromide respond to its ß rays. X-rays produce only a weak glow, so that despite its attractive optical properties the substance is not capable of replacing the expensive platinum salt in technology.

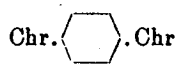
The substance shares with barium platinum cyanide the remarkable property that the splendid fluorescence is linked only to the solid state. Its solutions fluoresce only very weakly. The alcohol solution was considered more closely; initially thought non-fluorescing, it only revealed a distinct (blue) fluorescence when we used quartz vessels and an iron arc as a light source. The solution had to be greatly diluted, finally reaching the concentration n/10,000. /520

8. Once the existence of auxochrome-like chromophores was established, I pursued the associated question of whether such research might not be continued and expanded completely independent of considerations of fluorescence. It can indeed, and the experience accumulated with styryl and cyan-styryl shows the way, once one understands what the special effects of a group acting simultaneously chromophorically and auxochromically would be.

Remember that none of the known auxochromes can produce color when chained to the ring in benzene. Proceeding from there, first let us study only those chromophores whose single inclusion in benzene likewise yields no appreciable color. This assumption applies for both styryl and cyan-styryl, for like stilbene, α-phenyl cinnamic acid nitrile is also pure white. Now we compare the following compounds containing para-state substituents (let the symbol "chr" mean such a chromophore), on the basis of the auxochrome rules.



Type I



Type II

In type I the strong auxochrome $N(CH_3)_2$ is confirmed quite normally compared to the chromophore, irrespective of whether the latter has auxochromic properties or not; for these properties can of course have no coloring reverse action on the $N(CH_3)_2$ group, since the group is not a chromophore.

The situation is different for type II. If the symbol "chr" is a usual chromophore, there is no interaction between the two substituents that would significantly change the color.[11] p-Dinitrobenzene is as little characterized by deeper coloration as is nitrobenzene. But if the chromophore simultaneously has auxochromic functions, one substituent acts on the other like any other auxochrome upon a chromophore, inciting it to a deeper coloring. Consequently, in type II compounds, the appearance of deeper coloring indicates the presence of auxochromic functions of the chromophore. /521

[11]The benzene ring inserted between the chromophores seems indeed to hinder color development here. Recall that glyoxal is yellow but terephthal aldehyde is white. Likewise, benzil is yellow and p-dibenzoyl benzene white.

The assumption for this rule, let me repeat, is that each compound containing the chromophore only once is still colorless. Otherwise we can only draw conclusions after closer investigation of the color changes and absorption shifts produced by adding the second substituent.

Comparing types II and I yields indications of the order of magnitude of the auxochromic function. If the chromophore has no auxochromic function, the above indicates that compound I will be considerably more deeply colored than compound II. p-Nitro dimethylaniline is intense yellow, and dinitrobenzene nearly colorless. But if the chromophore has highly developed auxochromic functions, the picture may very well reverse, and compound II be the more deeply colored. Hence we can say that a chromophore whose type II compounds are as deeply as or more deeply colored than those of type I has a very strong auxochromic function, on the order of magnitude of the efficacy of the true auxochrome $N(CH_3)_2$.

9. Using the two rules just developed, I checked numerous chromophores and indeed found auxochromic functions in a number of them. Since fluorescence phenomena were found repeatedly, the table below, which summarizes the results in the meantime, includes these phenomena. All indications refer to the solid substances, and to observation behind the blue pane for fluorescence. /522

The foundation substances containing the chromophore only once are all known, except for the fifth.[12] This absent substance, benzal cyanacetophenone, was therefore produced, and was

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[12]Benzal indandione is yellowish, according to its discoverers. W. Wislicenus and A. Kötzle, A. 525, 75 (1889). The same is true of my preparation. In all comparisons, the color contrasts were selected great enough that this yellowish tone is without significance.

found to be white as the assumptions require.

The nomenclature of various substances listed in the table is rather difficult, and to make it less cumbersome I propose the name "phthalal" for the residue $C_6H_4(CH:)_2$ of phthalaldehydes. Accordingly, e.g. the type II compound is called "terephthalal-di-cyanacetophenone" with the fifth chromophore and "terephthalal-di-indandione" with the sixth. Other phthalal compounds not contained in the table will be reported on later.

	Chromophor[a]	$(CH_3)_2N.C_6H_4.Chr$		$Chr.C_6H_4.Chr$	
		Farbe[b]	Fluorescenz[c]	Farbe[b]	[c]Fluorescenz
1.	$CH:CH.C_6H_5$	weiß[d]	ziemlich stark grünlichblau[e]	blaßgelb[f]	stark gelbgrün[g]
2.	$CH:C(CN)C_6H_5$	citronengelb[h]	intensiv leuchtend grüngelb[i]	citronengelb[h]	leuchtend gelb[j]
3.	$CH:C(CN)CO_2.C_2H_5$	orange	leuchtend orange[k]	grünlich-hellgelb[l]	leuchtend gelbgrün[m]
4.	$CH:C(CN)_2$	ziegelrot[n]	stark orangerot[o]	gelb[p]	stark gelb[q]
5.	$CH:C(CN)CO.C_6H_5$	ziegelrot[n]	leuchtend ziegelrot[r]	orangegelb[s]	sehr schwach, undeutlich gelb[u]
6.	$CH:C<\begin{matrix}CO\\CO\end{matrix}>C_6H_4$	tiefrot[t]	mäßig purpurrot[v]	orange	stark orange[w]

Key:
a. chromophore
b. color
c. fluorescence
d. white
e. rather strong greenish blue
f. pale yellow
g. strong yellow-green
h. lemon yellow
i. intense brilliant green-yellow
j. brilliant yellow
k. brilliant orange
l. greenish light yellow
m. brilliant yellow-green
n. brick red
o. strong orange-red
p. yellow
q. strong yellow
r. brilliant brick red
s. orange-yellow
t. deep red
u. very weak, indistinct yellow
v. moderate purple-red
w. strong orange

10. The auxochromic efficacy of the chromophores listed in the table is very uneven. If one applies the second of the

rules developed above, one finds that only the first and second chromophore -- i.e., styryl and cyan-styryl, as found before -- can stand alongside the $N(CH_3)_2$ group. With the other four chromophores, the type II color is not nearly as deep as that of type I, proving that their auxochromic properties are much less than those of the $N(CH_3)_2$ group.

The table also gives rise to a general remark concerning principles. The efficacy of an auxochrome can be measured by the shift towards longer wavelengths occurring in the fluorescence of the benzene nucleus. This is naturally allowed only under the condition that one compares only substances without chromophores or only substances with the same chromophore, and precisely this prerequisite is not provided when one compares auxochrome-like chromophores with one another. If one ignores this prerequisite, one gets into grave errors. For example it would be quite mistaken to conclude from the fact that distyrylbenzene fluoresces yellow-green and terephthalal-di-indandione orange, i.e. at a longer wavelength, that therefore the 6th chromophore is more strongly auxochromic than styryl. The substances do not contain the same chromophore, and their comparison thus says nothing about the extent of auxochromic functions. /523

11. To get more detailed information on the degree of auxochromic character in the 5th and 6th chromophore, I used suitable nitro- and methoxyl derivatives for comparison. p-Nitrobenzal cyanacetophenone and p-nitrobenzal indandione were produced. The first is light yellow, the other greenish yellow. Thus both are doubtless more deeply colored than p-nitro anisol, which of course is white. This shows that in both chromophores the auxochromic function is still somewhat greater than that of methoxyl.

One gets the same result in a completely different way. If one considers type I compounds, in which not the $N(CH_3)_2$ group

but methoxyl, OCH_3, is introduced as a true auxochrome, and if one finds that they are less deeply colored than the type II, then, as above, one can again conclude that the auxochromic function of the chromophore is of the same or greater order of magnitude as that of methoxyl.

p-Methoxybenzal cyanacetophenone is only light yellow, while terephthalal-di-cyanacetophenone is orange-yellow. Type II thus has the deeper color. The same situation is found with the compounds of the 6th chromophore. p-Methoxybenzal indandione is lemon yellow, and terephthalal-di-indandione orange. Consequently in this second way, quite independent of the first, one finds that the auxochromic function of the 5th and 6th chromophore is on the order of that of methoxyl.

Experimental Part

(in collaboration with A. Jeutter)

Except for distyrylbenzene, all substances needed for the study could be produced by condensing certain aldehydes with certain methylene compounds. In addition to methylene compounds, whose condensation capacity is known, we also worked with cyanacetophenone, and found that it also reacts very easily with aldehydes and belongs among the especially reactive methylene compounds. Condensation occurs in an alcohol solution upon addition of some alkali or piperidine, or in some cases by merely boiling the solution. Below we describe only those condensations yielding the substances of interest here.

The employed aldehydes are almost all from the aromatic series and mostly condense with good yields. Significant difficulties develop only with nitro aldehydes, for which /524 the reaction sometimes only runs partway in the desired direction, yielding slightly resinous and more deeply colored byproducts. After the condensations with terephthalaldehyde, we also

tried some with glyoxal, since here we could expect products in which the middle benzene ring present in type II is absent, thus eliminating its influence. The experiment was successful, yielding 1,4-dicyan-1,4-dibenzoyl butadiene.

p-Distyrylbenzene: $C_6H_5.CH:CH.C_6H_4.CH:CH.C_6H_5$.

To the magnesium chloride solution prepared from 4.5 g benzyl chloride, 0.9 g magnesium and 20 cc ether, a solution of 1.5 g terephthalaldehyde in 80 cc ether was added gradually. The mixture, from which a yellow substance immediately precipitated, was heated a short while longer in the water bath, and then mixed with water and then acetic acid to remove the magnesium hydroxide. The supernatant ethereal solution was treated with ammonia, washed with water and dried with potash. Upon evaporation it yielded a viscous, yellowish oil, which when let stand for some time became cloudy, precipitating small crystals. This carbinol was not examined further, but subjected immediately to water fractionation, for which the following procedure proved most worth recommending. The oily product is heated for 1/4 hour with 10 g freshly distilled acetyl chloride, then the excess acetyl chloride is distilled back off and the remaining viscous mass is slowly heated to 270°C in a paraffin bath. The reaction indicated by incipient boiling around 140°C is complete when a removed sample solidifies immediately upon cooling. The solid cake produced by cooling is the desired distyrylbenzene, which we completely purified by triple recrystallization from heavy benzene (boiling point 160-180°C). Yield 2.2 g.

0.1864 g substance: 0.6386 g CO_2, 0.1087 g H_2O.
$C_{22}H_{18}$. Calculated C 93.62, H 6.38.
Found C 93.44, H 6.53.

Distyrylbenzene forms pale yellow crystals that melt at 258°C and dissolve with great difficulty in alcohol but somewhat

more easily in benzene. The substance is also only slightly soluble in most other solvents; but it is extensively accepted by chloroform and in this solution presents a splendid blue-violet fluorescence. The other solutions fluoresce less, in accord with their much weaker concentration.

To be sure that the substance has the indicated constitution, we oxidized it. As expected, this yielded terephthalic acid and benzoic acid. 0.2 g of the substance were boiled with 5 cc purified glacial acetic acid, and gradually mixed with 0.5 g chromic acid, initially completely dissolving the substance. Upon longer boiling a white substance precipitated. After /525 cooling we diluted with 20 cc water, boiled it again, hot-filtered the precipitate and washed it thoroughly with hot water. Since the substance was still colored greenish by chromium salts, it was extracted with soda solution and precipitated again from this liquid with hydrochloric acid. It precipitated as a voluminous, white mass, recognizable as terephthalic acid. The coincident benzoic acid appeared in the acetic-acid filtrate containing chromium -- which developed when the raw terephthalic acid was drawn off -- and could be removed with ether. The ethereal solution was washed with water to remove acetic acid, then shaken out with soda solution, the soda solution was separated from the ether, and treated again with fresh ether after acidulation. Upon evaporation in a vacuum desiccator, the last step yielded a white product easily identified as benzoic acid.

Dicyan Distyrylbenzene: $C_6H_5.C(CN):CH.C_6H_4.CH:C(CN).C_6H_5$.

The solution of 1.3 g terephthalaldehyde and 3.5 g benzyl cyanide in 40 cc alcohol was mixed with 10 drops of strong caustic potash solution, turning it yellow-brown and precipitating small amounts of a yellow product. To increase this product, we boiled the mixture another 20 minutes in the water bath and

then crystallized it several times from glacial acetic acid. Yield 2.4 g.

0.1814 g substance: 0.5758 g CO_2, 0.0822 g H_2O. -- 0.2137 g substance: 15.8 cc N (17°C, 747 mm).

$C_{24}H_{16}N_2$. Calculated C 86.75, H 4.82, N 8.43.

Found C 86.57. H 5.07, N 8.55.

The substance forms yellow crystals that melt at 242°C and are very hard to dissolve in most solvents. Their fluorescence has already been described.

Terephthalal-Di-Cyanacetic Ester:

$C_2H_5O_2C.C(CN):CH.C_6H_4.CH:C(CN).CO_2C_2H_5$.

Three drops of piperidine were added to 1.2 g terephthal-aldehyde and 2 g cyanacetic acid ethyl ester dissolved in 30 cc alcohol. The liquid became cloudy and solidified shortly into a yellowish slurry of crystals, which were drawn off, washed with alcohol and recrystallized twice from heavy benzene. Yield 2.1 g.

0.1895 g substance: 0.4617 g CO_2, 0.0869 g H_2O. -- 0.2113 g substance: 16.3 cc N (16°C, 737 mm).

$C_{18}H_{16}O_4N_2$. Calculated C 66.67, H 4.94, N 8.64.

Found C 66.45, H 5.13, N 8.83. /526

The product forms greenish light yellow needles that melt at 201°C and dissolve very poorly in alcohol, somewhat more readily in benzene and rather easily in chloroform. In contrast to the solid substance, the solutions showed no fluorescence in experiments to date.

Terephthalal-Di-Malonitrile: $(CN)_2C:CH.C_6H_4.CH:C(CN)_2$

A solution of 1.3 g terephthalaldehyde and 1.3 g malonitrile in 50 cc alcohol was heated to the simmer for several hours. It precipitated a yellow substance which was recrystallized from glacial acetic acid after washing out with alcohol. Yield 1.7 g.

0.1629 g substance: 0.4376 g CO_2, 0.0398 g H_2O. -- 0.1718 g substance: 37.6 cc N (23°, 737 mm).

$C_{14}H_6N_4$. Calculated C 73.04, H 2.61, N 24.35.
Found C 73.26, H 2.73, N 24.48.

The compound decomposes at 212°C, is yellow and dissolves only very little in most solvents. It is more readily soluble in acetone.

Terephthalal-Di-Cyanacetophenone:
$C_6H_5.CO.C(CN):CH.C_6H_4.CH:C(CN).CO.C_6H_5$.

1.3 g terephthalaldehyde and 2.9 g cyanacetophenone were dissolved in 30 cc alcohol and condensed with a few drops of piperidine. The liquid solidified over a quarter hour into a slurry of orange-yellow crystals, which were washed out with alcohol and recrystallized twice from anisol. Yield 3.2 g.

0.1749 g substance: 0.5417 g CO_2, 0.0645 g H_2O. -- 0.1992 g substance: 13.0 cc N (18°C, 731 mm).

$C_{26}H_{16}O_2N_2$. Calculated C 80.41, H 4.12, N 7.22.
Found C 80.26, H 4.11, N 7.36.

The substance melts at 224°C, is orange-yellow and extremely poorly soluble in solvents.

Terephthalal-Di-Indandione: $C_6H_4 \cdot \overset{CO}{\underset{CO}{\cdot}} C:CH.C_6H_4.CH:C \cdot \overset{CO}{\underset{CO}{\cdot}} C_6H_4$.

A solution of 0.3 g terephthalaldehyde and 0.8 g indandione in 20 cc alcohol was heated to boiling for several hours and the precipitated yellow produce was recrystallized twice from nitrobenzene after washing out with alcohol. Yield 0.9 g.

0.1789 g substance: 0.5237 g CO_2, 0.0596 g H_2O.

$C_{26}H_{14}O_4$. Calculated C 80.00, H 3.59.

Found C 79.84, H 3.73. /527

The orange needles melt above 300°C and are very poorly soluble in the usual solvents.

Benzal-Cyanacetophenone: $C_6H_5.CH:C(CN).CO.C_6H_5$.

Two drops of piperidine were stirred into a mixture of 5.6 g cyanacetophenone and 4.2 g benzaldehyde in 15 cc alcohol. With gentle heating, complete dissolution occurred, and after a few minutes the new product began to precipitate; it was then crystallized from alcohol. Yield 7.5 g purified product.

0.2091 g substance: 0.6309 g CO_2, 0.0887 g H_2O. -- 0.2123 g substance: 11.7 cc N (21°C, 732 mm).

$C_{16}H_{11}ON$. Calculated C 82.39, H 4.76, N 6.01.

Found C 82.29, H 4.72, N 6.15.

The product is obtained in white crystals that melt at 84°C and dissolve rather poorly in ether and cold alcohol, but easily in chloroform. The alcohol solution shows an absorption band in the ultraviolet. A yellow solution results with concentrated sulfuric acid.

p-Methoxy-Benzal-Cyanacetophenone: $CH_3O.C_6H_4.CH:C(CN).CO.C_6H_5$.

This compound was obtained by the same method. When caustic potash solution is used instead of piperidine the yield is also nearly quantitative. The compound forms light yellow needles, MP 104°C, dissolving orange with concentrated sulfuric acid.

0.2113 g substance: 0.6012 g CO_2, 0.0970 g H_2O. -- 0.2237 g substance: 10.7 cc N (17°C, 739 mm).

$C_{17}H_{13}O_2N$. Calculated C 77.57, H 4.98, N 5.33.
Found C 77.60, H 5.13, N 5.39.

p-Dimethylamino-Benzal-Cyanacetophenone:
$(CH_3)_2N.C_6H_4.CH:C(CN).CO.C_6H_5$.

From 3 g dimethylamino benzaldehyde and 3 g cyanacetophenone, using 5 g piperidine, purified substance was obtained by crystallization from benzene. It melts at 162°C, is brick red and dissolves easily in chloroform, less well in alcohol and very poorly in ether.

0.2104 g substance: 0.6034 g CO_2, 0.0174 g H_2O. -- 0.2161 g substance: 19.1 cc N (17°C, 747 mm).

$C_{18}H_{16}ON_2$. Calculated C 78.26, H 5.80, N 10.15.
Found C 78.22, H 5.71, N 10.23. /528

The solution of this substance in concentrated hydrochloric acid is colorless. When gaseous hydrogen chloride is passed over the red crystals, they become white, demonstrating that the substance forms a white salt with hydrochloric acid. It dissolves yellow in concentrated sulfuric acid.

p-Nitro-Benzal-Cyanacetophenone: $NO_2.C_6H_4.CH:C(CN).CO.C_6H_5$.

The condensation of p-nitrobenzaldehyde with cyanaceto-

phenone, when piperidine is used, provides only a moderate yield. Heating the reaction mixture is not recommended, since it results in a different orange-red, hard-to-dissolve substance. Caustic potash solution works much like piperidine. After recrystallization the product forms light yellow flakes that melt at 140°C.

0.2033 g substance: 17.8 cc N (13°, 728 mm)
$C_{16}H_{10}O_3N_2$. Calculated N 10.07. Found N 9.95.

p-Nitro-Benzal-Indandione: $NO_2.C_6H_4.CH:C\begin{matrix}CO\\CO\end{matrix}C_6H_4$.

This substance results easily and in a good yield if one briefly boils an alcohol solution of p-nitro-benzaldehyde and benzalindandione. Since it is very poorly soluble in alcohol, it precipitates even at simmering heat and produces violent shaking of the liquid. By recrystallizing from benzene one gets it in the form of fine, greenish-yellow needles, MP 229°C. Sometimes it contains a white byproduct whose formation can be avoided by simply melting the two components together without solvents.

0.2095 g substance: 9.6 cc N (14°, 737 mm).
$C_{16}H_9O_4N$. Calculated N 5.02. Found N 5.25.

1,4-Dicyan-1,4-Dibenzoyl-Butadiene:
$C_6H_5.CO.C(CN):CH.CH:C(CN).CO.C_6H_5$.

We dissolved 2.9 g glyoxal bisulfite in an excess of diluted hydrochloric acid, heated the liquid in the water bath, evaporated it until dry and extracted the residue with alcohol. In the alcoholic extract, 2.9 g cyanacetophenone were dissolved. The solution, mixed with a few drops of piperidine, soon precipitated yellowish crystals which became white after four crystallizations from glacial acetic acid.

0.2008 g substance: 0.5647 g CO_2, 0.0714 g H_2O. -- 0.1838 g substance: 14.5 cc N (21°C, 736 mm).

$C_{20}H_{12}O_2N_2$. Calculated C 76.92, H 3.85, N 8.97.
Found C 76.71, H 3.98, N 8.87.

The substance decomposes without melting between 170° and 175°C. The fact that it is white is of particular interest and proves that in terephthalal-di-cyanacetophenone the middle benzene ring plays an important role in coloring. The significance of the middle ring also appears with distyrylbenzene, which is of course yellow, while diphenylbutadiene, which does not have this middle ring, is still pure white.

<u>p-Dimethylamino-Cyanostilbene</u>: $(CH_3)_2N.C_6H_4.CH:C(CN).C_6H_5$.
(with E. Meyer)

This compound, so interesting because of its splendid fluorescence, is easy to produce and forms with a good yield when dimethylamino benzaldehyde is condensed with benzyl cyanide by means of potash. It recrystallizes from alcohol in the form of yellow flakes that melt at 136°C. It dissolves poorly in alcohol and ether, but rather easily in benzene, acetone, pyridine and particularly chloroform.

0.1996 g substance: 0.6009 g CO_2, 0.1142 g H_2O. -- 0.1858 g substance: 18.4 cc N (13°, 735 mm).

$C_{17}H_{16}N_2$. Calculated C 82.26, H 6.45, N 11.29.
Found C 82.20, H 6.41, N 11.32.

The substance is a rewarding field for physical fluorescence research. Its fluorescence capacity depends on temperature and is considerably less at 100°C than at usual temperature.